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Oxidative Dehydrogenation of Methanol to Formaldehyde[1]

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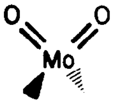
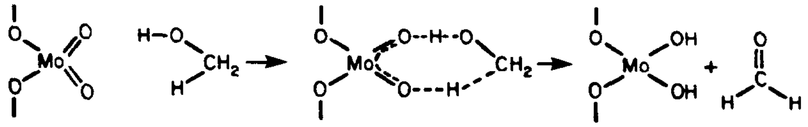
Thermochemical results from *ab initio* quantum chemical calculations (generalized valence bond) are used to examine the reactions mechanism for $H_3COH + \frac{1}{2}O_2 \rightarrow H_2CO + H_2O$ as catalyzed by MoO_3. We find that surface dioxo sites



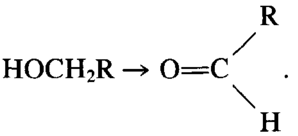
are critical to activating the methanol, but we find that the single-site single-step proposal



is not favorable ($\Delta H \approx +31.5$ kcal). Our conclusion is that an important catalytic site involves two adjacent surface *dioxo units* (the *dual dioxo site*), with each dioxo site extracting one H in a sequence of steps. The required dual dioxo site exists on the (010) surface of MoO_3 but does not exist on the other low index surfaces. This mechanism is supported by atmospheric pressure experimental studies which indicate that $MoO_3(010)$ is selective for CH_2O products. A detailed sequence of reaction steps and the associated thermochemistry is proposed.

INTRODUCTION

The mild catalytic oxidation of aliphatic alcohols ($C_nH_{2n+1}OH$) over simple metal oxides usually leads to the formation of carbonyl compounds, $C_2H_{2n}O$. Thus, primary alcohols are selectively oxidized to aldehydes



$$HOCH_2R \rightarrow O{=}C\begin{matrix} R \\ \\ H \end{matrix} \quad . \qquad (1)$$

A classic example of this is the oxidative dehydrogenation of methanol to formaldehyde over the molybdenum trioxide catalyst, MoO_3,

$$CH_3OH + \tfrac{1}{2}O_2 \xrightarrow[\text{(200–300)°C}]{MoO_3} CH_2O + H_2O \qquad (2)$$

Pure MoO_3 exhibits ~100% *selectivity* but has low activity (*1*). Addition of Fe_2O_3 to MoO_3 increases the *activity*, with an optimal Mo:Fe ratio of 1.7 (*1*). Molybdates as well as complex oxide catalysts, K_2MoO_4, $CaMoO_4$, $CoMoO_4$, $Cr_2(MoO_4)_3$, $Fe_2(MoO_4)_3$, and $Bi_2(MoO_4)_3$, are also used for the selective formation (~95%) of formaldehyde from methanol, with the activation energy for these processes varying between 10 and 20 kcal/mol at 275°C (*1*). Because of the extreme industrial importance of formaldehyde for plastics, dyes, etc., the highly selective reaction (2) has been the focus of much study (*2–5*).

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Most of the information concerning the mechanism of reaction (*2*) to date has been extracted from a variety of infrared spectroscopy, mass spectroscopy, and kinetic isotope studies (*1–9*). The following concepts are generally accepted regarding the oxidation of methanol to formaldehyde over MoO_3:

(a) The first step consists of dissociative adsorption of methanol to yield surface methoxy and surface hydroxyl species. This has been established by infrared studies which show evidence of a *nonvolatile* surface species with bands at 2925, 2825, and 1440 cm^{-1} assigned to methyl asymmetric stretch, symmetric stretch, and deformation vibrational frequencies (C–H bend), respectively, and a band at 1065 cm^{-1} due to the C–O stretch (*7*). These band assignments have been confirmed by Sleight *et al.* (*13*).

(b) The rate-determining step is the breaking of a C–H bond of the surface methoxy species. This has been established by changes in product distribution from the starting products CH_3OH versus CH_3OD and from CH_3OH versus CD_3OD (*3, 6*).

(c) The activation energies for oxidation of methanol over MoO_3 and $Fe_2(MoO_4)_3$ are in the range 16–20 kcal/mol (*1*).

(d) The catalysis by both supported and unsupported single crystals of MoO_3 crystals having a variety of geometries indicates that the basal crystal face [(010) surface] of MoO_3 is responsible for forming formaldehyde H_2CO, while the side surface [(100)] and apical surfaces [(001) plus (110)] lead to methylal $CH_2(OMe)_2$ and dimethyl ether $(CH_3)_2O$, respectively (*4*).

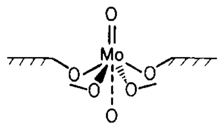
(e) Mo═O centers have been identified by a number of workers as possible dehydrogenation centers believed to be important in *mild* oxidation (*4, 5, 8, 9*).

Despite the progress indicated above, there is little known about the *detailed* sequence of reaction steps or the thermochemistry of methanol oxidation over metal oxide catalysts. Thus, one does not know what surface *sites* are required for selective formation of H_2CO and which sites lead to formation of the acetal, ether, or CO_2. Our goal is to develop a sufficiently detailed understanding of these mechanisms that one could design new catalysts that would be more selective or more active.

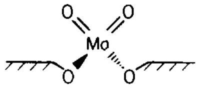
As a basis for the mechanistic considerations of the mild oxidation of methanol by molybdate catalysts, we have carried out a series of *ab initio* quantum chemical calculations [generalized valence bond (GVB) and configuration interaction (CI)] on models of various active sites. These studies provide some new insights concerning mechanisms that we believe move us closer to the above goal. We first outline the relevance of the emerging paradigm concerning transition metal oxides and then examine some details of the mechanism.

SPECTATOR EFFECTS

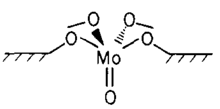
The molybdate systems lead to bulk structures involving either octahedral or tetrahedral coordination of oxygens about each Mo. As a result, one would expect the most stable surface configurations for such molybdates to be as indicated in



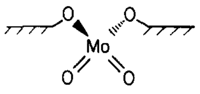
1



2



3a



3b

where **1** and **3a** derive from bulk octahedral sites and **2** and **3b** derive from bulk tetrahedral sites. Here each single-bonded O makes a strong single bond to a second Mo (typical bond distances of ~1.9 Å), whereas the oxygen involved in the double bond (Mo═O) is bonded only to the one Mo (typical bond distances of 1.67 to 1.73 Å in the bulk); the next closest oxygen is typically 2.2 to 2.4 Å. All four cases involve

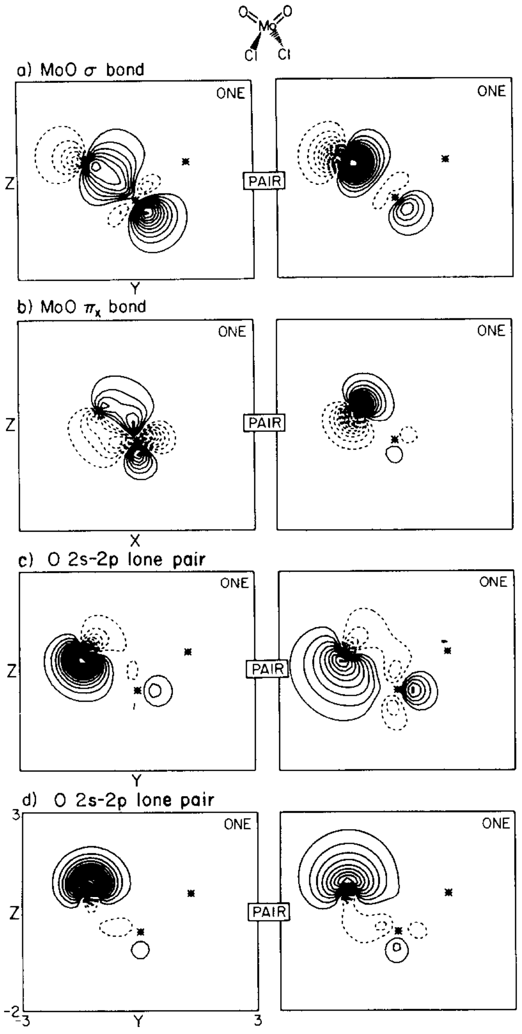
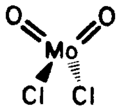


Fig. 1. GVB orbitals for the electron pairs involving the left Mo=O double bond in species **2**. Dotted contours indicate negative amplitude. Increments between contours are 0.050 a.u.; the zero contour is *not* shown.

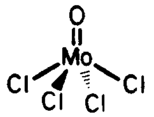
Mo^{VI} centers and cases **1** and **2** both involve surface Mo=O double bonds. However, we find that species **1** and **2** lead to extremely different chemistry. This remarkable difference arises from the *spectator oxo effect* (*10, 11*), as discussed below.

Figure 1 shows the bonding for



as a model of the dioxo species **2** (with each Cl modeling a bridging oxygen). Here we see that each Mo=O bond has the form of a covalent double bond involving spin pairing of two singly occupied Mo *d* orbitals and two singly occupied O *p* orbitals. Denoting the Mo=O axis as z and the MoO$_2$ plane as yz, the Mo–O σ bond involves Mo d_{z^2} and O p_z (leading to an overlap of 0.78), while the Mo–O π bond involves Mo d_{xz} and O p_x (leading to an overlap of 0.64). Two such bonds require four Mo electrons in four orthogonal Mo *d* orbitals. On the other hand, the two Mo–Cl bonds (modeling single bonds to the two bridging oxygens in molybdates) involve a large amount of ionic character with some $5s$–$5p$ character on the Mo. Thus the Mo^{VI} center in **2** should be best visualized in terms of ionic bonds to the two bridging oxygens, while the Mo=O bonds should be considered as covalent double bonds. The requirement of four singly occupied *d* orbitals for the two Mo=O bonds leads to an O=Mo=O angle of 106° (the π bonds would prefer 90°; the σ bonds, 125°) (*11*). In addition to the two singly occupied oxygen *p* orbitals involved in the Mo=O bond, each oxygen has four valence electrons in two nonbonding orbitals (mixture of O $2s$ and O $2p_y$).

The bonding is quite different when there is only one multiple bonded oxygen, as indicated in Fig. 2 (the orbitals are for



where each Cl models a bridging oxygen of **1**). Here there are *two* π bonds between Mo and O. Thus, taking the Mo=O axis as z, there is a π bond involving Mo d_{yz} and O p_y and a π bond involving Mo d_{xz} and O p_x. In addition, the Mo has a total of four partially ionic bonds to the four Cl, accounting then for the six Mo valence electrons (in this description the Mo d_{z^2} orbital is empty). The two Mo=O π bonds require two singly occupied $p\pi$ orbitals on the oxygen (p_x and

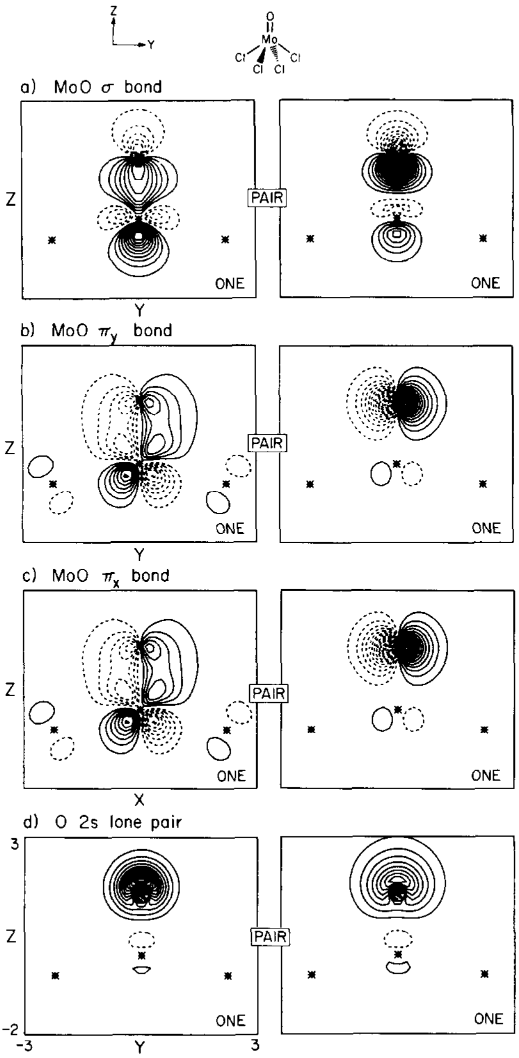
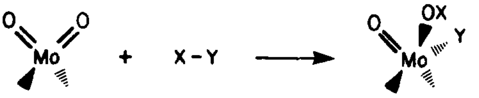


Fig. 2. GVB orbitals for the electron pairs involving the triple bond for species **1**. (Same plotting conventions as in Fig. 1.)

p_y), leaving four electrons for the O 2s and O 2p_z orbitals. With two electrons in O 2p_z and none in Mo d_{z^2}, we obtain a Lewis base–Lewis acid bond in the σ system, leading to a net Mo–O bond involving *six electrons* (four from oxygen and two from Mo). The result is a *partial triple bond* that is much stronger than the double of bond of **2**. Why can species **2** not make two such partial triple bonds? The requirement is *two* singly occupied metal π orbitals (π_x and π_y) for *each* super double bond so that there are just not enough Mo π orbitals to go around for **2**. This is analogous to the difference between O=C=O with two *double* bonds and C=O with a partial triple bond about twice as strong.

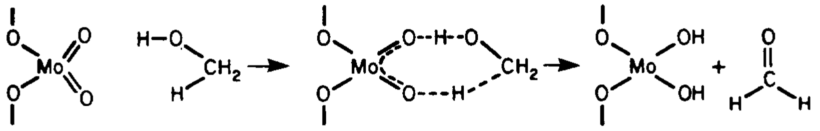
When chemistry occurs at one Mo=O bond, for example,



4 **5** (3)

the extra Mo=O bond of **4** would appear to be a spectator to the reaction, but in fact it helps *promote* the reaction. The spectator Mo=O bond changes from a double bond in **4** to a super double bond in **5** when chemistry occurs at the *other* Mo=O bond. This results because the Mo–OX and Mo–Y bonds in **5** are σ bonds, neither requiring Mo $d\pi$ orbitals. As a result, the spectator Mo=O bond in **5** can sequester both Mo $d\pi$ orbitals for its own purposes, yielding two π bonds plus the donor–acceptor σ bond for an overall *partial triple bond.* Thus the spectator oxo group is stabilized by the reaction, and hence *the spectator oxo group promotes reaction at the adjacent double-bonded group.* Such spectator oxo effects have proved important in homogenous metathesis catalysis by Mo (*10, 16, 17*) and we suggest below that they are critical in oxidative dehydrogenation. For surface species such as **3a** and **3b**, the Mo=O bonds are protected from direct attack; however, the exposed part of the Mo should act as an electrophile (Lewis acid) that could stabilize the physisorption of species such as CH_3OH.

Indeed, Trifiro *et al.* (*5*) have long maintained that Mo=O double bonds are important in oxidation catalysts and have suggested that the dioxo center **2** should be the important center since it can simultaneously extract both hydrogens from methanol,



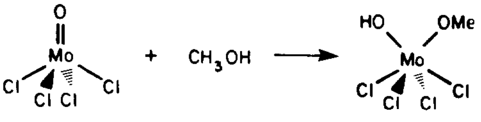
(4)

$\Delta H \approx +31.5$ kcal/mol

Although the simple pictures in (4) make the process *look* plausible, it is in fact very endothermic, $\Delta H \approx +31.5$ kcal. Of course, this mechanism is also inconsistent with the experimental evidence of adsorbed methoxide (*vide supra*). The problem is that (4) involves loss of two strong Mo=O π bonds, but the resulting two unpaired electrons on the Mo are not utilized for any two strong bonds (formally, the Mo is changed from Mo^{VI} where all six valence electrons are involved in bonds to Mo^{IV} where only four electrons are involved in bonds).

THE MECHANISM

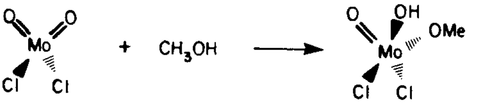
Considering the interaction of CH_3OH with the likely surface species, **1**, **2**, and **3** of MoO_3, we find the following energetics (12) for the simplest one-center process,



(5)

1

$\Delta H_5 = +22$ kcal/mol
$\Delta G_5 = +33$ kcal/mol
(25°C)



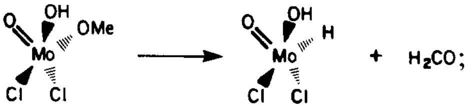
(6)

2 **6**

$\Delta H_6 = -9$ kcal/mol
$\Delta G_6 = +2$ kcal/mol
(25°C)

Thus, species **1** with a partial triple bond is *not* effective in activating methanol; however, due to spectator oxo stabilization, *species* **2** *can activate CH_3OH in a one-center process.*

From (4) we see that the Mo–O partial triple bond in (6) cannot extract the H from the bound methoxy to form formaldehyde. The remaining possibility for one-center process would be β-hydride elimination of formaldehyde from **6**



(7)

6

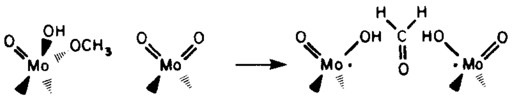
$\Delta H_7 = +30$ kcal/mol
$\Delta G_7 = +10$ kcal/mol
(300°C)

However, our model system (7) leads to a high barrier for this process. Because of uncertainties concerning possible surface configurations on MoO_3, we must still consider β-hydride elimination as a viable alternative; however these results led us to consider other alternatives.

Consequently, we will now consider whether a *second* Mo site

(8)

might play a role in the catalytic process. If two dioxo units are arranged so that chemisorption of the CH_3OH to form a methoxy unit places a CH bond sufficiently close to one of the oxo bonds of the *second dioxo unit*, then cleavage of the C–H bond of the chemisorbed methoxy group in **6** to form CH_2O can be facile.



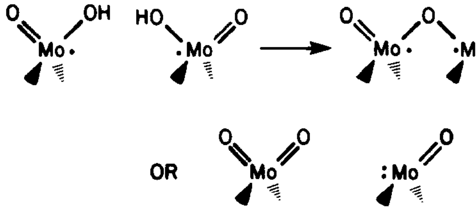
(9)

$\Delta H_9 = +6$ kcal/mol
$\Delta G_9 = +6$ kcal/mol
(300°C)

[In (9) the OH groups probably bridge to an adjacent Mo center and the CH_2O is considered complexed to the surface.]

This process is favorable only because it is promoted by the spectator oxo group on this dioxo unit.

After completion of step (9), subsequent steps involve desorption of formaldehyde, associative desorption of H_2O, e.g.,



(10)

and replenishment of the surface with bulk oxide to reconstruct the active site.

Thus we suggest that *selective oxidative dehydrogenation of CH_3OH to CH_2O requires a dual set of adjacent* dioxo units with an overall scheme as indicated in Fig. 3. For each dioxo unit, one of the two oxygens can extract a hydrogen, with the other oxygen providing the spectator oxo stabilization. The spectator oxo effects are crucial in making the chemisorption step (6) exothermic and keeping the CH chemisorption step (9) only slightly endothermic. In this description one would expect the CH bond cleavage (9) to be the rate-determining step [as proved in recent experiments (*5*)]. There should be an additional barrier to desorbing H_2O [step (10)] after formation and desorption of $H_2C{=}O$. Indeed, this is found in temperature-programmed reaction studies (*7*).

Now the question is, does MoO_3 have a surface with the requisite configuration having adjacent dual oxo sites? Indeed, as indicated in Fig. 4, examination of the crystal structure (*14*) of MoO_3 shows that the (010) surface has exactly the configuration needed for the steps in Fig. 3 and Scheme I. On the other hand, the other low index faces of MoO_3 do *not* have the requisite combination of dual units. This conclusion that dual dioxo units are essential for the catalytic dehydrogenation of CH_3OH is strongly supported by the experimental studies of the Lyon group (Tatibouët and Germain) (*4*). In the presence of O_2, they find that $MoO_3(010)$ is highly selective for

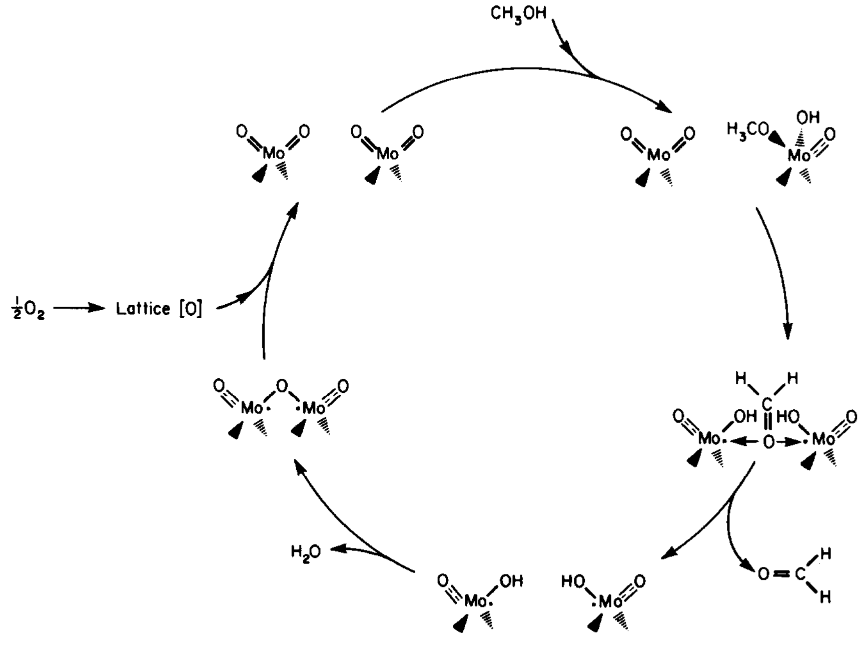


FIG. 3. The sequence of reaction steps for the dual dioxo catalytic site.

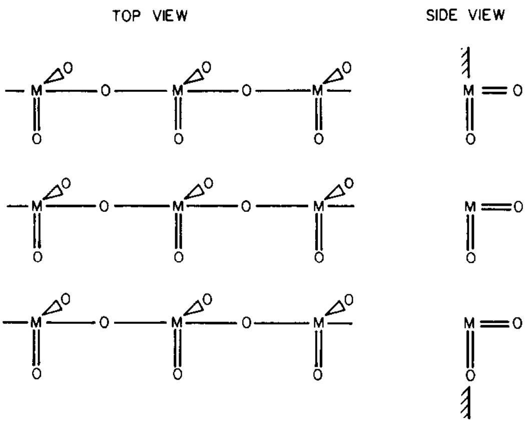


Fig. 4. The (010) surface of MoO_3. Oxygen above plane is in y direction and is double-bonded to Mo in plane.

formation of H_2CO, whereas $MoO_3(100)$ leads to methylal, and $MoO_3[(001) + (101)]$ are bifunctional [leading to H_2CO and $O(CH_3)_2$].

The (100) surface is shown in Figs. 5 and 6, where we see that there are exposed (isolated) dioxo units and buried ones (as in **3b**). Tatibouët and Germain suggest that it is the bifunctionality that is responsible for the production of methylal. The low index faces (001) and (101) are expected to be less stable, and it is not clear what the reconstructed surface is like. However, the observed lack of selectivity is certainly consistent with the expected multifunctionality.

From Fig. 5 we see that there are two plausible forms for the Mo(010) surface. The one shown in Fig. 4 leads to oxo units pointing out of the surface and would appear to be the most stable surface. Alternatively, shaving the top layer leads to a surface structure as shown in Fig. 5. In this case the oxo units point along the surface and down, exposing Lewis base sites. This might physisorb CH_3OH but does not appear plausible for chemisorption. We speculate that this surface may be stabilized under environments with low O_2 pressure

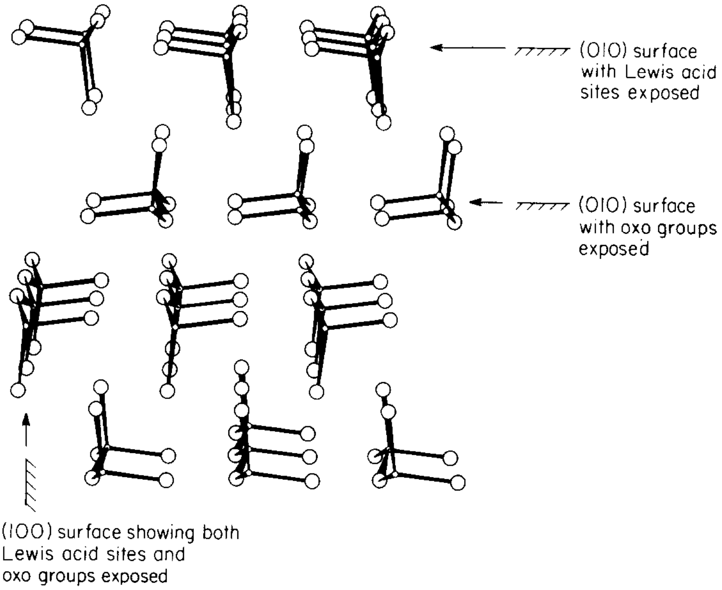
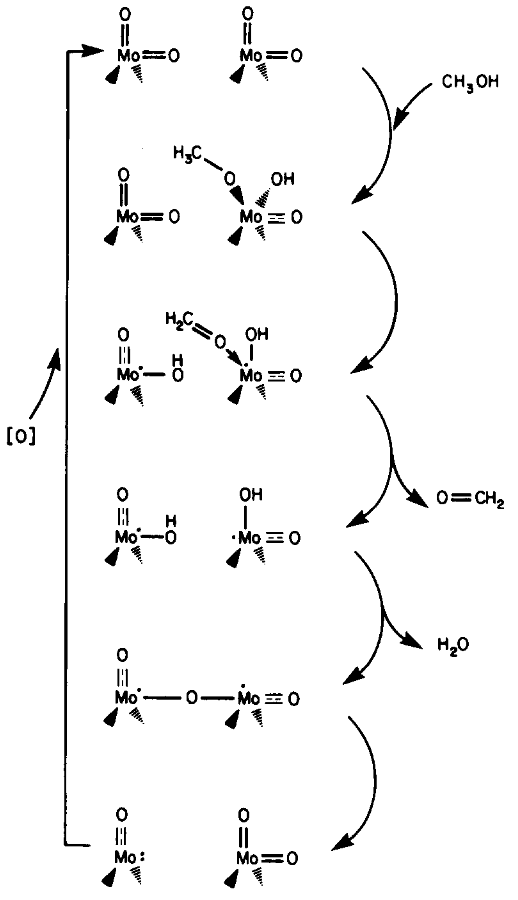


Fig. 5. Side views of the (010) and (100) surfaces of molybdenum trioxide, MoO_3. Plots were made using the PLUTO program (Sam Motherwell, University Chemistry Laboratory, Cambridge, England) as follows: Packing range: $a = -1.5$ to 1.5; $b = 0.0$ to 1.0; $c = 0.0$ to 1.0. Scale factor: 15 (15 mm ≡ 1 Å). Mono 1500 (single plot with perspective drawing as seen from a distance of 1500 mm). The view shown is the $MoO_3(010)$ surface whose image has subsequently been rotated about the fixed plotter axes x,y,z (z-axis rotation, 90°; x-axis rotation, 83°).



Scheme 1. The mechanism for oxidative dehydrogenation on the dual dioxo site of MoO_3 (010).

(vide infra). If so, this would explain the results of the Lyon group who find no reaction with CH_3OH unless O_2 is present.

DISCUSSION

It has sometimes been suggested (*15*) that the (010) surface of MoO_3 may be nonreactive compared with other surfaces because it has no broken chemical bonds. Our mechanism suggests that this simple reasoning is inadequate for $MoO_3(010)$, and indeed the experiments of Ref. (*4*) provide strong evidence that $MoO_3(010)$ is the important surface for formation of H_2CO.

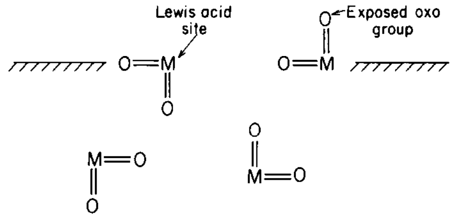
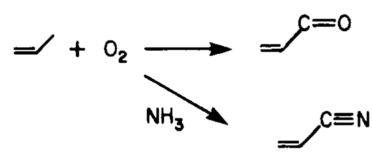


Fig. 6. Schematic diagram of $MoO_3(100)$ side face. For this bifunctional face there are pairs of alternating Lewis acid sites and exposed oxo group sites.

The specific new mechanism proposed here, involving a dual dioxo catalytic site, is susceptible to many experimental tests. We expect that such interplay between theory and experiment will promote the development of a much more detailed understanding of the fundamental chemical mechanisms of heterogeneous catalytic reactions. We believe that sites involving collections of surface dioxo units are also important in selective oxidation and ammoxidation reactions (*18*).



After submission of our original manuscript, a paper appeared (*19*) that may seem to contradict both the conclusions from the experimental studies at Lyon (*4*) and our theoretical studies. Using large single crystals of MoO_3 with large exposed basal planes (010), the (*19*) group exposed these surfaces with up to 10^5 L of CH_3OH at room temperature and observed no changes in the UPS. This might seem to contradict the results of the Lyon group; however, it should be noted that the Lyon group also found no reaction unless O_2 was present with the CH_3OH (they also used higher temperatures, 200–300°C). A second consideration is whether UPS is sufficiently sensitive to detect submonolayer adsorption of CH_3OH on $MoO_3(010)$. Studies on polycrystalline MoO_3 indicated reaction to form CH_2O under conditions where the UPS does not change (*19*).

ACKNOWLEDGMENTS

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